Manchester Metropolitan University

Selection of a suitable ligand for the supercritical extraction of gold from a low-grade refractory tailing

L.D. van Dyk [a], G. Mawire [a,b], J.H. Potgieter [a,c] and M. Dworzanowski [a]

[a] DRD Gold Extraction Group, School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private Bag X3, Wits 2050, South Africa

[b] School of Civil and Mechanical Engineering, Curtin University, Bentley, WA 6102, Australia

[c] Department of Natural Science, Faculty of Science and Engineering, Manchester Metropolitan University, Chester Street, M1 5GD, Manchester, UK

Abstract

Reprocessing tailings for gold recovery is generating new low-grade refractory secondary tailings. Unlocking gold trapped within these secondary tailings potentially holds additional economic value. In this study, the use of supercritical carbon dioxide ($scCO_2$) at 100 bar and 40 °C for gold extraction from such a secondary gold tailings sample (0.27 g/t) was investigated. The research identified and screened the following ligands as suitable extractants for gold in $scCO_2$, i.e. 3-(trifluoromethyl)-phenyl-thiourea (TPT), 1,1,1-trifluoro-2,4-pentanedione (TFA), betaine bis(trifluoromethylsulfonyl)imide ([Hbet][TF_2N]), 4-methyl-4H-1,2,4-triazole-3-thiol (MHTT) and hexafluoroacetylacetone (HFA). Results from screening experiments showed that extraction of gold for all ligands in the presence of a tri-n-butyl phosphate-nitric acid adduct (TBP-HNO_3) as oxidant exceeded 50% after 18 h, with the highest extraction offered by [Hbet][TF_2N] (82% after 24 h). A comparative study, where no $scCO_2$ was present, showed that the presence of $scCO_2$ offered a distinct advantage in extraction.

Keywords: supercritical CO_2, gold, low-grade tailings, silicates, ligands

1   Introduction

Gold mining and processing in the Witwatersrand basin has generated a considerable amount of waste over the years. More than 95% of the millions of tonnes of ore processed every year is disposed of in the form of waste rocks and mine tailings. The gold grade in these tailings is very low, usually less than 0.5 g/t. Despite these low grades, the sheer volume of tailings makes the recovery of even a fraction of this gold, potentially lucrative. The exploration or recovery of gold from secondary ores, such as tailings, presents several advantages, as it requires less capital investment compared to raw ore processing. Tailings can also be an environmental burden and the management of large volumes of tailings is becoming expensive, thus rekindling the interest in the processing of tailings. Gold tailings are generally classified as refractory because the gold occurs within minerals that consume unacceptable quantities of reagents and conventional leaching practice delivers poor gold extraction. In most instances, the gold grains are encapsulated within the crystal matrix of gangue minerals, making them inaccessible for further conventional leaching and results in reduced recoveries [1, 2, 3]. To improve gold leaching from refractory gold sources such as secondary tailings, it is necessary to look to alternative extraction processes. One such process is the use of supercritical fluids in the extraction of gold.

Processes that involve supercritical fluids (SCF) operate at conditions above the critical temperature (Tc) and pressure (Pc) of the substance. For CO_2, the vapour-liquid line terminates at the critical point, which means that beyond that point the vapour and liquid phases become indistinguishable [4]. Supercritical carbon dioxide ($scCO_2$) thus possesses gas- and liquid-like properties and can be described as either a highly condensed gas with remarkable transport capabilities or a highly mobile liquid with excellent solvent strength characteristics. Carbon dioxide is a commonly used SCF because of its low critical temperature (31.1 °C) and pressure (74 bar) [5].

It is the liquid-like density that enables the solvation of many materials in $scCO_2$ and the gas-like viscosity which affects the rate of mass transfer. These two factors are influenced by temperature and pressure. With increasing pressure, the carrying capacity, i.e. density of the fluid is enhanced, however this result in a lower diffusivity coefficient as a result of increased viscosity. With increasing temperature, the transport properties, i.e. diffusivity coefficient is enhanced, but this compromises the density of the fluid. Therefore, the net result of the two opposing effects can be positive or negative, depending on which is the more dominant effect at the given conditions [6, 7]. Besides, it is also an attractive SCF solvent as there is minimum waste generation, separation of solutes is easy, which makes the fluid recyclable and easy to recover from a solute, it is safe to use (non-toxic), inexpensive, readily available and it offers a solution for CO_2 utilisation [8]. Metal ions are insoluble in $scCO_2$ due to a neutral charge requirement, and the weak interaction between carbon dioxide and metal ions [9]. $scCO_2$ therefore only acts as a carrier solvent for the chelating and/or oxidising agents in the metal extraction process.

Direct extraction of metals from solids with complexing agents in $scCO_2$ has recently attracted interests in the metal processing industry [10]. Precious metals including gold can be processed in $scCO_2$ by oxidation and subsequent leaching with a complexing agent. Wang and Wai [11] reported the dissolution of metallic gold using a TBP-HNO_3 complex as an oxidizing agent and a β-diketone, hexafluoroacetylacetone (HFA) as a chelating agent. Studies by Glennon et al. [12] reported the extraction of Au(III) from cellulose paper using fluorinated macrocyclic reagents based on calixarene molecular baskets in $scCO_2$. In their work, extractions above 90% were reported using one of the fluorinated thiourea derivatives tested, and 78% was the highest extraction efficiency achieved when using thiourea calixarenes. Gold can also be eluted from activated carbon under supercritical conditions. Otu [9] and Van Zyl et al. [13] used tributylphosphate for the elution of aurocyanide in a $scCO_2$ environment and were able to
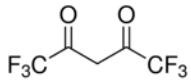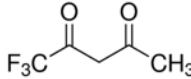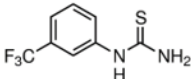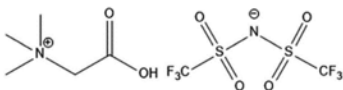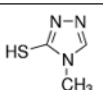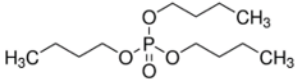
recover significant amounts of gold. While literature on the extraction of gold in $scCO_2$ exists, the research is limited, and no work has been reported on the extraction of gold from naturally occurring matrixes.

This research explores the initial technical feasibility of gold extraction in $scCO_2$ from secondary tailings from the processing plant at ERGO, operated by DRDGOLD Ltd, by identifying and assessing different ligands. The ERGO plant treats surface tailings, sand dumps, and slime dams left behind by gold mining operations across the Witwatersrand basin. The total gold recovery obtained in the process is around 37%. More than 50% of gold in the process feed is associated with sulfidic minerals, of which the greatest portion is pyrite, with approximately 29% of the gold. During reprocessing, the ore is separated into two processing streams, a high-grade sulfide-rich stream (obtained by flotation concentration) and a low-grade stream consisting of high-grade leach tailings and flotation tailings. The solid product from the process is a siliceous rich material in which gold is trapped and impossible to leach further with conventional cyanidation. The extraction of gold from this secondary tailing material is the focus of the research within our group as it still has potential economic value worthwhile exploring, and serves as the motivation behind this study.

1.1 Ligand Selection

$scCO_2$ is effective in dissolving nonpolar and slightly polar compounds, thus making it a poor solvent for polar compounds due to charge neutralisation. Consequently, it is necessary to investigate the in-situ chelation of metal ions with CO_2-philic ligands. The selection of ligands, and in this case an oxidising agent, is very important. A variety of chelating agents have been tested for metal chelation in $scCO_2$ and these include dithiocarbamates, β-diketones, organophosphorus reagents, and macrocyclic ligands [14]. Table 1 provides a list of the ligands selected for this study, their abbreviated names, and their structures.

Table 1 Ligands selected for investigation in this study

Class	Full name	Abbreviation	Structure
β-diketones	hexafluoroacetylacetone	HFA	
	1,1,1-Trifluoro-2,4-pentanedione	TFA	
Thiourea derivatives	3-(Trifluoromethyl)phenyl Thiourea	TPT	
Ionic liquids	betaine bis(trifluoromethylsulfonyl)imide	[Hbet][TF$_2$N]	
Thiol	4-methyl-4H-1,2,4 Triazole-3-Thiol	MHTT	
Organophosphorus	Tributyl phosphate	TBP	

A β-diketone is a molecule containing two ketones separated by one carbon atom. The most common, simple β-diketone is acetylacetone and most of the derivatives of β-diketones are based on substituting methyl groups with different functional groups on it [15]. Fluorinated β-diketones have been used in conjunction with organophosphorus ligands in synergistic leaching. HFA and/or TFA forms soluble adducts with TBP in scCO$_2$ and these adducts have successfully been used in the leaching of various metals such as Cu, Pd, U, La, Lu, and Eu [16, 17, 18]. TFA which has a similar complexing functional group as HFA (dicarbonyl functional group), was selected for comparison. HFA which has two CF$_3$ substituents is expected to have a higher extraction efficiency because of the additional electron-withdrawing effect of fluorine-containing group [17]. Acetylacetone is believed to not have the same synergistic effect with TBP and has low solubility in scCO$_2$, compared with its analogues containing fluorine substituents [16].

The thiol MHTT was selected in this study because it is a sulfur-containing ligand, and in general sulfur-containing ligands are highly selective for Au (III). Vidhate and co-workers [19] used 4-(methoxybenzylideneimino)-5-methyl-4H-1,2,4-triazole-3-thiol (MBIMTT) for the extraction of gold from an acidic solution in chloroform. The loading capacity of 10 mL, 0.1 M MBIMTT was found to be 6.5 mg of gold (III). The similar properties of $ScCO_2$ to chloroform made MHTT which has similar properties to MBIMTT, a potential ligand for this study.

Thiourea has successfully been used for gold extraction under acidic conditions and forms cationic complexes [20]. Thiourea has certain advantages, including low sensitivity to base metals (Pb, Cu, Zn, As, Sb), and residual sulfur in calcines. However, it has poor stability and can be easily converted to other forms, which hinders its effectiveness in gold processing [21, 20]. Thiourea derivatives, on the other hand, have lower reagent consumption and do not form elemental sulfur, but they are suspected to be carcinogenic. 1-Phenyl-2-thio-3-(2-hydroxyethyl) urea (N, N′-disubstituted-thiourea), was tested by Aydin et al. [22] on pure gold powder and relatively high gold extractions (>95%) were reported in a sulfuric acid solution with the ferric ion as oxidant.

Neutral sulfur-containing organic compounds are selective extractants for noble metals and thiourea derivatives have been investigated as extractants for platinum group metals, silver, and gold [23]. It has also been tested in $scCO_2$, giving positive results. Simpler fluorinated 3, s-di(trifluoromethyl) phenyl thiourea derivatives were reported by Glennon and co-workers [12] to be effective ligands for gold extraction in $scCO_2$. These researchers have done extensive work on gold extraction with thiourea derivatives in $scCO_2$ from spiked cellulose paper and they showed the effect of temperature and pressure on extraction. Glennon et al. [24], through careful choice of donor atoms, reported the extraction of gold without modifiers in $scCO_2$ with fluorinated calixarenes and thiourea derivatives. Simpler fluorinated bis-(trifluoromethyl)

phenyl thiourea derivatives proved to be better ligands than non-fluorinated thiourea derivatives at lower operating pressure [12].

Ionic liquids (ILs) are molten salts at ambient conditions that are completely composed of organic cations and inorganic or organic anions. They have several chemical and physical advantages over conventional chemicals and molecular organic solvents due to their ionic nature and low toxicity. Among others, some of the advantages of ILs are negligible flammability and vapour pressure, high solvation ability, high selectivity, and that they can be used as designer solvents. Some of the physicochemical properties that can be altered are density, viscosity, and melting point, making them flexible for different applications [25].

Work done by Oraby and Eksteen [26] on the successful extraction of gold from sulfidic ores using glycine, prompted the selection of the ionic liquid [Hbet][TF$_2$N] for scCO$_2$ extraction of gold. This IL contains a glycine cation derivative, trimethylglycine, or commonly known as betaine. The use of ILs as ligands or complexing agents to directly solvate gold from an ore or its zero-valent state has not been reported yet. Whitehead et al. [27] reported the use of the IL, 1-Butyl-3-methylimidazolium hydrogen sulfate (BmimHSO$_4$), as a carrier solvent to replace sulfuric acid in thiourea leaching. Other studies on gold processing in ionic liquids reported in literature are liquid-liquid extraction and electrodeposition of gold [28]. Various authors [29, 30, 31] have shown that the trifluoromethanesulfonimide anion [TF$_2$N]$^-$ interacts well with scCO$_2$. The IL was mostly used in a two-step process where scCO$_2$ was used to recover the IL by stripping the metal ligands off. IL-scCO$_2$ interaction can result in reduced viscosity of the IL [32] consequently enhancing the extraction efficiency in the process. It should be noted that the mutual miscibility of ILs with scCO$_2$ is not clearly designated and it is an area under research. Various authors [33, 34, 35] have reported on the solubility of ILs in scCO$_2$ and some authors have reported on the solubility of CO$_2$ in ILs and not the former in the latter [32].

[Hbet][TF$_2$N] is therefore an interesting IL as it has a CO$_2$-philic anion and a gold complexing cation, and is easily synthesised from a metathesis process from readily available reagents [36].

The majority of research on [Hbet][TF$_2$N] has been focussed on the extraction of metals from their oxides in an aqueous environment and demonstrates its ability to solubilise oxides of rare earth, uranium(VI), zinc(II), cadmium(II), mercury(II), nickel(II), copper(II), palladium(II), lead(II), manganese(II) and silver(I) [36, 28]. Experimental work by our group to test the proof-of-concept idea to use [Hbet][TF$_2$N] for gold extraction, showed that 48 % and 40 % of gold could be extracted from a sulfide-rich tailings' concentrate ore without scCO$_2$ at 75 °C for 24 h at a solid to liquid ratio of 1 g ore: 5 mL liquid, a pH of 1.3 and using H$_2$O$_2$ and HNO$_3$ as oxidants, respectively. This was the first time that an IL ([Hbet][TF$_2$N]) was used as a ligand for gold extraction directly from ore, proving the proof-of-concept idea.

Tributyl phosphate (TBP) as an HNO$_3$-TBP adduct was used as the oxidant in this study. Sinclair et al. [37] showed that this adduct can leach rare earth metals on its own while other researchers [38, 39, 40], also reported its use as a ligand. Subsequently, the influence of the adduct as an extractant was also studied.

2   Materials and methods

2.1   Chemicals

The ionic liquid [Hbet][TF$_2$N] was synthesised as reported by Mawire and van Dyk [36] from the two salts, betaine hydrochloride (99%) and lithium bis(trifluoromethylsulfonyl)imide (99%), both sourced from Sigma-Aldrich. The chemicals, 3-(trifluoromethyl)-phenyl-thiourea (TPT 97%), 1,1,1-trifluoro-2,4-pentanedione (TFA 98%), 4-methyl- 4H-1,2,4 triazole-3-thiol (MHTT 98%), hexafluoroacetylacetone (HFA 98%), tri-n-butyl phosphate (TBP 97%), nitric acid (HNO$_3$ 55%) were also sourced from Sigma-Aldrich. All chemicals were used as supplied with no further purification.

A tri-*n*-butyl phosphate-nitric acid (TBP-HNO$_3$) adduct was used as an oxidizing agent and was prepared using an adapted method from Enokida et al. [41]. 5 mL of 11.7 M HNO$_3$ was mixed with 23 mL of 97 % tri-*n*-butyl phosphate (TBP) in a conical flask. The mixture was stirred vigorously for 15 min, followed by centrifuging until phase separation occurred. After phase separation, the TBP-HNO$_3$ phase was pipetted off. A titrimetric analysis on the adduct with 1 M NaOH gave a HNO$_3$ concentration of 2.75 M in the TBP-HNO$_3$ complex. A FTIR analysis of the prepared sample and a reference 97 % TBP solution confirmed the synthesis of the adduct as TBP(HNO$_3$)0.7(H$_2$O)0.7.

2.2 Gold-bearing samples

The gold-bearing samples were collected from DRDGOLD Ltd ERGO plant and two representative samples were obtained, one from the plant feed and another from the plant tailings. All extraction experiments were performed on the plant tailings sample.

The plant feed and plant tailings samples were collected by taking samples using sample cutters and composites were produced to take variability into account. Gold speciation, gold grain size distribution, gold liberation, and gold association were investigated for the plant feed sample. This information was used to make inferences about the association of gold in the plant tailings.

Representative samples of the collected plant tailings for use in the scCO$_2$ extraction experiments were prepared using standard techniques as described by Wills [42]. The gold head grade and other metal content of the sample were obtained by solid acid digestion, followed by inductively coupled plasma (ICP) analysis of the solution.

2.3 Experimental setup

The supercritical fluid extraction setup used in the research is presented in Figure 1. The experimental setup comprises of a CO$_2$ cylinder (1) connected to a Maximator air driven pneumatic pump (7) for supercritical CO$_2$ generation, connected to a 400 mL high pressure,

jacketed SS316 autoclave with an inside Hastelloy C extraction basket (12) to protect the reactor against corrosion. The inside and outside temperature of the vessel was monitored and controlled with a GEFRAN 600 temperature controller (20) equipped with two type K thermocouples, one located on the outside of the vessel and the other in the reactor thermo-well (24). A magnetic stirrer (IKA C-MAG HS 7) (11) was used for stirring with a bar magnet. The system was operated in batch mode.
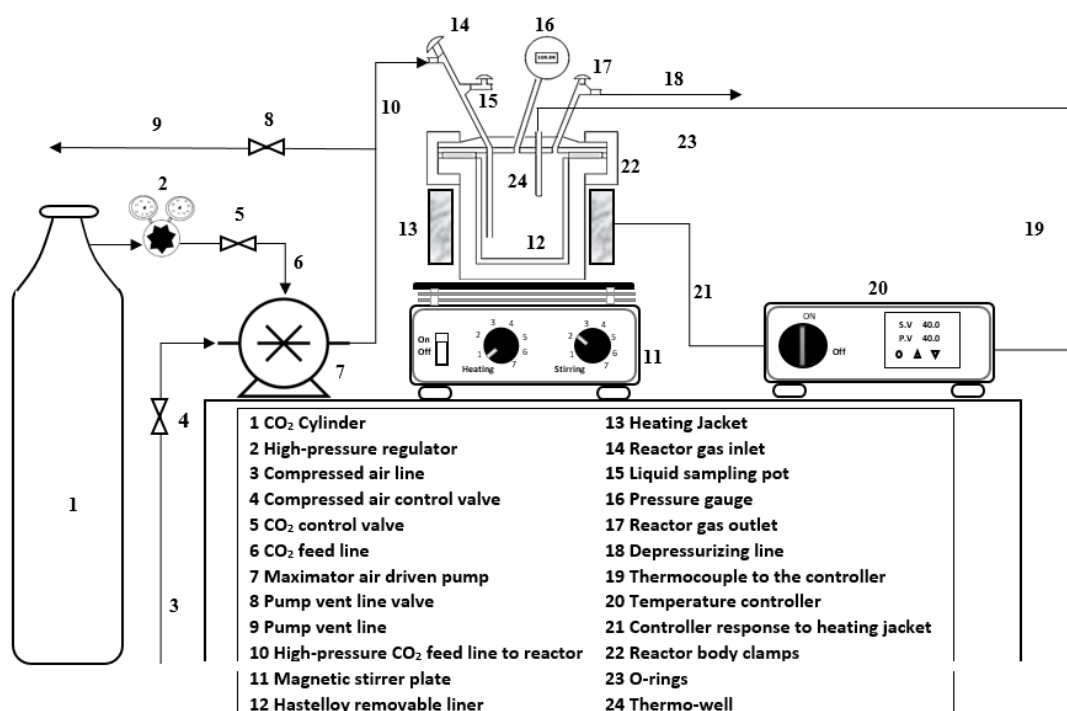

Figure 1 Supercritical fluid extraction unit

2.4   Ligand Screening experiments

A mass of 20 g of dried tailings was charged into the Hastelloy basket together with 28 mL of the synthesised HNO_3-TBP adduct and a corresponding amount of ligand ([Hbet][TF_2N], HFA, TFA, MHTT, and TPT, TBP). The experiments were run at 100 bar and 40 °C. After a set time (6, 12, 18, 24 h), the pressure was reduced to atmospheric pressure, and the slurry was removed from the reactor and filtered (Whatman® grade 540 filter paper). The solid residue was washed thoroughly with deionised water and dried in an oven. After drying the solid residue samples

were digested using the Anton Paar Microwave Digestion System. Digestion was done using 1 g samples (in duplicate) of the residue material in an acid solution comprising HCl (9 mL), HNO_3 (3 mL), HF (1 mL), and H_3BO_3 (8 mL). After digestion, a pipetted amount (2 mL) of the liquid was diluted with deionised water to 10 mL and the solution was analysed on an Agilent 200 series AAS for metal gold concentration. The percentage extraction was defined as:

$$\% \; Extraction = \left(\frac{Initial \; mass \; of \; gold \; in \; solid \; sample - mass \; of \; gold \; in \; solid \; residue}{initial \; mass \; of \; gold \; in \; solid \; sample} \right) \times 100 \quad (1)$$

The solid residue after $scCO_2$ gold extraction was also prepared for XRD analysis by using a back-loading preparation method and was analysed with a PANalytical Aeris diffractometer with a PIXcel detector and fixed slits with Fe filtered Co-Kα radiation. The phases were identified using X'Pert Highscore Plus software. The relative phase amounts (weight %) were estimated using the Rietveld method.

Considering same mass ratio of dried tailings to extractant system, additional comparative extraction experiments were performed at atmospheric conditions (no $scCO_2$) to determine the effect of $scCO_2$ on the extraction of gold.

All extraction experiments were conducted in duplicate and the average values are reported in the results. Margins of error were found to be within 3% at 90% confidence level.

3   Results and Discussion

3.1   ERGO plant tailings sample

The concentration of the main metals and gold in the ERGO plant tailings sample are presented in Table 2. The sample contains a multitude of metals, with iron and aluminium the most prevalent species. The measured gold concentration was 0.27 g/t and presents a substantial

amount of gold if one considers that the plant processes approximately 2 million tonnes of ore per month.

Table 2 Metal composition (only main metal species and Au) in the ERGO plant tailings

	Al	K	Ca	Ti	Mg	Fe	Cu	Au
g/t	12134	1248	2994	69.6	3420	19226	43.89	0.27

An XRD analysis on the plant tailings sample showed that it consisted mostly of quartz (79.39 %) and muscovite (13.43%). Details of the other mineral species are given in Table 6.

The association of gold with various mineral groups of the feed material entering the carbon in leach (CIL) section of the plant which produces the plant tailings exit stream is presented in Table 3. Before cyanidation of this process stream, the gold is mostly associated with sulfide minerals and some free gold exists. It is assumed that the free gold and some of the gold associated with the sulfide minerals will leach in the CIL section and the remainder will report to the plant tailings. As only 3.5 % of this feed is found in the flotation concentrate, and the rest (96.5 %) is subjected to direct cyanidation, some inferences can be made about the gold available for leaching from the ERGO plant tailings sample based on the plant feed analysis. If one assumes that the readily available gold is leached in the cyanidation process, then gold available for extraction from the ERGO plant tailings sample is essentially locked.

Table 3 Gold association with mineral groups in the feed to the CIL section of the ERGO plant

Mineral type	Associated Gold (%)
Free gold	6.5
Sulfides	54.7
Silicates	18.8
Oxides	12.0
Uranium minerals	8.0

3.2 Ligand Screening

Figure 2 shows the extraction of gold with time from the ERGO plant secondary tailings for different ligands in the $scCO_2$ system (HFA, TFA, TPT, MHTT, and [Hbet][TF$_2$N]). HNO_3 carried by TBP as an HNO_3-TBP adduct was used as the oxidant with all ligands. The extraction of gold in CO_2 was done at 100 bar and 40 °C, which is sufficiently above the T_c and P_c of CO_2 (31 °C and 74 bar) to create $scCO_2$ [5]. The choice of operating pressure and temperature was limited by the working pressure of the reactor and guided by a minimal energy usage requirement for isothermal operation.

From Figure 2 it is seen that initially, the gold extraction was fast for all the ligands under investigation, but the reactions slowed down significantly after about 10-12 h. The initial extraction rates (slopes) are high, indicating the leaching of possibly readily accessible gold. The leaching rates then slow down and reach plateaus representing the maximum amount (%) of extraction under these conditions.

The highest leaching was achieved with the IL [Hbet][TF$_2$N] with gold extraction of 82% after 24 h. The β-diketone HFA extracted the second-highest amount of gold after about 15 h (70%), while the other β-diketone, TFA, gave similar initial extraction rates to HFA, but with a lower total extraction (60%). It is interesting to note that after 12 h, similar extraction rates were obtained for the ligand TPT and TFA.
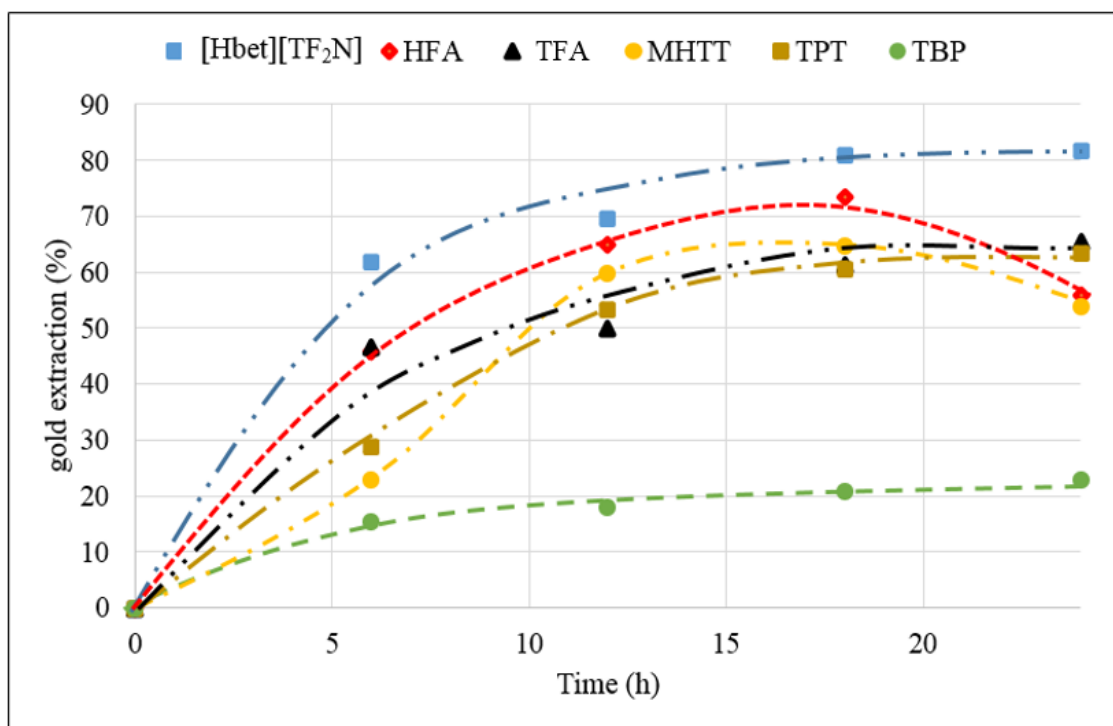

Figure 2 scCO$_2$ extraction of gold with different ligands at 100 bar and 40 °C

TPT and MHTT also gave extractions above 50% for gold. The extraction was very low when the adduct TBP-HNO$_3$ was used alone. The maximum extraction that could be reached after 12 h was approximately 20 %. The presence of the ligands in the leaching system enhanced the gold extraction significantly, confirming the positive influence of the ligands on gold extraction in the system. An analysis of variance (ANOVA) test was done to investigate if the use of a different ligand gave any significant difference. A single factor (ligand) test was done at 6, 12, 18, and 24 h, and the source of variation between groups is presented in Table 4. The null hypothesis (there is no significant difference in using different ligands on extraction) of equal

variances can be rejected because the p-value < 0.05, indicating the alternative hypothesis can be accepted and the variation observed with the use of different ligands is therefore significant.

Table 4 Analysis of variance (ANOVA) test results to show the significance of different ligands on gold extraction

time (h)	DOF	F-value	P-value	F-critical
6	5	1961	1.50×10^{-09}	4.38
12	5	10925	8.69×10^{-12}	4.38
18	5	2869	4.79×10^{-10}	4.38
24	5	9550	1.30×10^{-11}	4.38

It is generally not advisable to use long extraction times with supercritical fluids, as it diminishes the economic feasibility of the process. From the results, it can be observed that extending the extraction time beyond 18 h had no significant effect on gold extraction. The order of extraction of gold up to 18 h was found to be [Hbet][TF$_2$N] > HFA > MHTT > TFA > TPT and TBP. In-situ chelation of metal ions with CO_2-philic ligands is dependent on two factors, the ligand-CO_2 interaction, and the ligand extraction efficacy. A highly soluble ligand would be effectively carried to the reaction site by scCO$_2$ and its leaching will be dependent on the strength of the ligand. Future work by our group to establish the leaching mechanism which clearly shows the limiting step is underway. At a macroscopic level, it can be observed that highly soluble ligands had better extraction rates.

To enhance the economics, one might consider reducing the reaction time as the extraction rate is most prominent in the first few hours of extraction.

ICP analysis of the digested leach solid residue samples also showed that other metals were co-leached with gold (Table 5). This was expected and indicates that scCO$_2$ extraction with these ligands, even though effective for gold leaching, is not selective. Despite being non-selective, the ability of the systems to co-leach other species is necessary to access locked gold. In a process, these species will consume additional reagents and necessitate further separation for gold recovery. It can also potentially represent an additional revenue stream if the metal species can be recovered and sold.

Table 5 Extraction percentages of selected metals with various ligands in scCO$_2$ (24 h, 100 bar, and 40 °C)

Sample	Al (%)	K (%)	Ca (%)	Ti (%)	Mg (%)	Fe (%)	Cu (%)
HFA	20.85	9.70	80.27	26.08	30.63	50.07	51.22
TFA	17.25	9.90	83.36	12.86	34.27	54.61	65.85
TPT	29.39	21.31	79.36	31.61	35.15	51.75	59.43
[Hbet][TF$_2$N]	0.18	19.55	87.14	16.52	10.47	57.39	64.67
MHTT	23.68	29.29	37.93	9.27	28.80	28.46	52.85

An analysis of the feed to the CIL section (Table 3) shows that gold in this ore is occluded by various gangue minerals, implying that gold is not readily available for leaching.

To investigate the changes in the mineralogy before and after scCO$_2$ extraction with the different ligands, XRD analysis were performed on the plant tailing sample and the residue solid after scCO$_2$ extraction. The relative phase amounts (weight %) were estimated using the Rietveld method and the results are presented in Table 6.

Identified phases in the plant tailings before extraction includes quartz (SiO_2), muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$), chlorite ($(Mg, Fe)_6 (Si, Al)_4O_{10}(OH)_8$), talc ($Mg_3Si_4O_{10}(OH)_2$), chloritoid ($(Fe, Mg, Mn)_2Al_4Si_2O_{10}(OH)_4$), gypsum ($CaSO_4 \cdot 2H_2O$) and pyrite ($FeS_2$).

Table 6   Relative phase amounts (weight %) of the ERGO plant tailings and scCO$_2$ gold leaching solid residue samples after 24 h leaching (100 bar and 40 °C).

	Quartz	Chlorite	Muscovite	Talc	Chloritoid	Gypsum	Pyrite
Before Extraction	79.39	3.44	13.43	0.84	2.6	0.02	0.28
HFA	88.04	2.13	9.08	0.09	0.63	0.01	0.02
TFA	87.78	2.61	7.93	0.03	1.63	0.02	0
TPT	89.54	2.07	4.71	0.02	3.5	0.02	0.15
[Hbet][TF$_2$N]	89.66	2.77	6.21	0	1.34	0.02	0
MHTT	80.57	4.47	10.92	0.25	2.27	1.13	0.39

The XRD data presented in Table 6, coupled with the gold extraction graphs in Figure 2, show that leaching with the selected ligands in scCO$_2$ is a very effective way of extracting gold from this refractory tailings sample, and most of the host minerals are attacked by the ligands under investigation. With the supercritical fluids' gas-like mass transfer efficiency and liquid-like solvation abilities, it was hypothesised that as a carrier solvent, scCO$_2$ will carry the ligand/s and the oxidant to the active site of the reactant (gold). This enabled the extractants to penetrate through possible cracks in the minerals, and extract gold back to the bulk fluid media. The XRD information showed that, in a system where gold is encapsulated by sulfide minerals

(pyrite) and various silicate minerals, the SCF system would leach through the gangue mineral, exposing the unliberated gold grains for further dissolution.

It is expected that during the ERGO process, cyanidation would have leached all the readily available gold, leaving behind plant tailings in which gold is trapped inside mineral species resistant to attack by cyanidation, such as layered silicates and certain oxides like rutile [43, 3], effectively making it "invisible", and necessitating the breakup or dissolution of mineral species to liberate gold for extraction.

Clay minerals are typically layered silicates and some have significant negative charges, which are compensated by cations (usually K^+, Na^+, and Ca^{2+}) in interlayer sites. In silicate networks, dissolution would favour breaking of weaker bonds and structural defects could be formed when the linkage species (Al, Mg, K, and Fe) are released as a result of the attack of the host mineral [44, 45]. The linkage species could be released into solution because of their susceptibility to attack, as shown in Table 5. Consequently, gold encapsulated by layered silicate minerals could be solubilised. The cracks and deformities created also enable further penetration with $scCO_2$ fluid which possesses excellent transport properties. These diffusion avenues can enhance gold extraction from clay minerals. Thus, it is reasonable to assume that gold associated with this class of minerals, is leached under supercritical conditions with the various ligands under investigation.

Talc is typically hydrophobic [46, 47], and the interaction of $scCO_2$, which is non-polar, with this mineral may have facilitated its attack, as observed in Table 6. It is seen that for [Hbet][TF_2N] and TFA no pyrite remains, which indicates the extent of leaching by these ligands. An analysis of the Ergo plant feed revealed that rutile (TiO_2) was present at 0.6% per mass and identified as the major oxide (Table 3) associated with gold in the detailed modal mineralogy. Gold associated with rutile (TiO_2) in the ERGO plant feed was about 9 %.

Although rutile was not observable in the XRD data of the ERGO tailings sample (below XRD detection limit), Table 5 shows that Ti was leached into solution. It can therefore be assumed that these ligands were also able to extract gold associated with this mineral. Extraction with each ligand shows a significant reduction in muscovite, which indicates that each of them are capable of attacking this silicate mineral. Quartz showed great resistance to attack and it can be assumed that the ligands, even under supercritical conditions, are unable to attack the quartz mineral. Despite quartz being resistant to attack, the presence of micro-cracks in quartz particles can be exploited by the low viscosity $scCO_2$ which can penetrate these cracks and extract finely disseminated gold within quartz grains. After 18 h in the MHTT and HFA systems, preg-robbing effects seem to be experienced and this can be confirmed by the fact that these two ligands (Table 6) have the lowest reduction of the silicate minerals which are preg-robbers [48].

3.3 Comparison of $scCO_2$ leaching and leaching at atmospheric conditions

To confirm whether the presence of $scCO_2$ enhances the leaching ability of the ligands, the extraction of gold was also performed at ambient conditions without CO_2. The findings after 24 h of leaching are presented in Figure 3. For most of the ligands, except MHTT and TBP, the extraction was almost doubled under supercritical conditions. The ambient extraction of gold with MHTT was very high relative to the other ligands, and it did not improve much (~ 8% after 24 h) by adding $scCO_2$. The TBP only system also showed no significant improvement of gold extraction under supercritical fluid extraction (SFE)conditions.
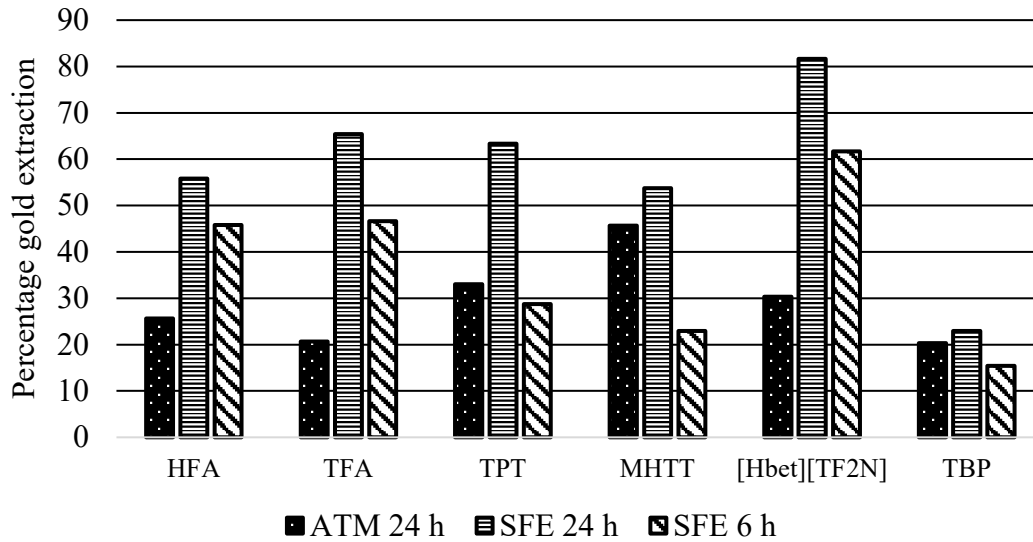
Figure 3 Comparison of gold extraction from ERGO plant tailings under supercritical fluid extraction (SFE) and atmospheric conditions (40 °C and 24 h)

A t-test was also conducted to confirm statistically the significance of adding supercritical CO_2 to the extraction system. The data from Figure 3 was split into two groups, group 1 SFE, group 2 ATM at 24 h. The paired sample t-test was then conducted on the groups, and from Table 7 it can be statistically concluded that SFE enhances extraction because the P-value < 0.05. A t-static > t-critical confirms that we can reject the null hypothesis (adding $ScCO_2$ does not affect the extraction process significantly). Thus SFE offers a distinct advantage over ATM leaching.

Table 7 t-Test: Paired Sample for Means; SFE vs ATM

t-Stat	P(T<=t) one-tail	t-Critical one-tail	P(T<=t) two-tail	t-Critical two-tail
3.49	0.009	2.015	0.017	2.571

The percentage extraction under supercritical conditions after 6 h for HFA, TFA, and [Hbet][TF$_2$N] is more than the percentage extraction under atmospheric conditions (no CO_2 present) after 24 h leaching (Figure 5). Supercritical conditions therefore offer improved

extraction kinetics over atmospheric conditions for certain ligands, confirming an advantage of supercritical conditions for leaching of gold.

4 Conclusions

The study shows that gold in a low-grade refractory tailings sample can be extracted efficiently under supercritical conditions compared to ambient conditions. Supercritical fluid extraction offers improved kinetics which is attributed to the enhanced transport properties exhibited by $scCO_2$. The various ligands are capable of leaching gold along with other metals into solution with the TBP-HNO_3 adduct as an oxidising agent. The dissolution is enhanced by the diffusivity of the $scCO_2$ which carry the ligands to the reaction surface and gold extractions for all ligand under investigation were above 50 % after 18 h. Layered silicate minerals and oxides like rutile can be attacked by various ligands carried by $scCO_2$, which makes gold locked and associated with these minerals, accessible for leaching, and reducing the preg-robbing effect of silicates.

The ionic liquid [Hbet][TF_2N] showed the highest extraction of gold of 82% after leaching for 24 h in a system containing $scCO_2$ and TBP-HNO_3. Ionic liquids with the assistance of a suitable oxidant can, given sufficient residence time, break down some of the minerals encapsulating residual gold values, notably pyrite, layered silicate minerals, and TiO_2 thus providing additional revenue in the retreatment of existing, low grade, stockpiled, tailings. This is an improvement considering that only 37% is currently being achieved in the ERGO process (high-grade stream 67% and low-grade 25%) using conventional cyanidation. This is the first time an IL was used in a supercritical fluid to extract a metal directly from its ore.

The successful demonstration of gold extraction in this system holds potential as a sustainable gold recovery process where the ionic liquid can be recovered and recycled. Ionic liquid recycling and reusability has been reported by various authors [49, 50]. Ongoing research will

focus on the optimization of the best cases identified in this study, as well as, the recovery and reuse of the ligand coupled with an economic evaluation of the conceptual design.

Future work

This work is part of an ongoing investigation by our group. Based on the knowledge gained from this research, investigating the extraction mechanism in order to optimise the extraction process is considered for future studies. Optimisation of selected ligands at different operating parameters to improve on the efficiency and economics of the process for the extension of these laboratory scale can result into a viable commercial process is a further study.

Acknowledgements

References

[1] H. Tutu, T. S. McCarthy and E. Cukrowska, The chemical characteristics of acid mine drainage with particular reference to sources, distribution and remediation: The Witwatersrand Basin, South Africa as a case study, Applied Geochemistry. 23 (2008) 3666–3684. https://doi.org/10.1016/j.apgeochem.2008.09.002

[2] S. Ndlovu, G. S. Simate and E. Matinde, Waste Production and Utilization in the Metal Extraction Industry, first ed., Taylor & Francis Group, Boca Raton, 2017.

[3] J. Marsden and l. House, The chemistry of gold extraction, second ed., Society for Mining, Metallurgy, and Exploration, Inc, Littleton, 2006.

[4] C. Erkey, Supercritical Fluids and Organometallic Compounds: From Recovery of Trace Metals to Synthesis of Nanostructured Materials, Volume 1, Supercritical Fluid Science and Technology, Elsevier, Amsterdam, 2011.

[5] C. M. Wai, A. S. Gopalan and H. K. Jacobs, Supercritical Carbon Dioxide Separations and Processes, American Chemical Society, Washington DC, 2003.

[6] F. P. Lucien and N. R. Foster, Phase behavior and solubility, In: P. G. Jessop and W. Leitner (Eds.), Chemical Synthesis Using Supercritical Fluids, Wiley-VCH Verlag GmbH, Weinheim, 1999, pp. 37-53.

[7] G. M. Schneider, C. B. Kautz and D. Tuma, Physico-Chemical Principles of Supercritical Fluid Science, In: E. Kiran, P. G. Debenedetti and C. J. Peters (Eds.), Supercritical fluids, Kluwer Academic Publishers, Dordrecht, 2000, pp. 31-68.

[8] C. Erkey, Supercritical carbon dioxide extraction of metals from aqueous solutions: a review, J Supercrit Fluids. 17 (2000) 259–287. https://doi.org/10.1016/S0896-8446(99)00047-9.

[9] E. O. Otu, Supercritical Carbon Dioxide Elution of Gold-Cyanide Complex from Activated Carbon, Sep Sci Technol. 32 (1997) 1107-1114. https://doi.org/10.1080/01496399708000949.

[10] X. Ding, Q. Liu, X. Hou and T. Fang, Supercritical Fluid Extraction of Metal Chelate: A Review, Crit Rev Anal Chem, (2017) 1547-6510. https://doi.org/10.1080/10408347.2016.1225254.

[11] J. S. Wang and C. M. Wai, Dissolution of Precious Metals in Supercritical Carbon Dioxide, Ind. Eng. Chem. Res. 44 (2005) 922-926. https://doi.org/10.1021/ie040198m.

[12] J. D. Glennon, J. Treacy, A. M. Keeffe, M. O'Connell, C. C. McSweeney, A. Walker and S. J. Harris, Extracting Gold in Supercritical CO2:Fluorinated Molecular Baskets and Thiourea Ligands for Au, In: A. S. Gopalan, C. M. Wai and H. K. Jacobs (Eds.) Supercritical Carbon Dioxide Separations and Processes, American Chemical Society, Washington D C, 2003, pp. 67-79.

[13] P. G. v. vanZyl, E. L. J. Breet and C. S. Williams, Recovery of $KAu(CN)_2$ from granular activated carbon using supercritical CO_2, J. Supercrit. Fluids. 47 (2008) 31-36. https://doi.org/10.1016/j.supflu.2008.05.008.

[14] A. Leybros, L. Hung, A. Hertz, D. Hartmann, A. Grandjean and O. Boutin, Supercritical CO_2 extraction of uranium from natural ore using organophosphorus extractants, Chem. Eng. J. 316 (2017) 196–203. https://doi.org/10.1016/j.cej.2017.01.101

[15] C. Pettinari, F. Marchetti and A. Drozdov, 1.6 - β-Diketones and Related Ligands, In: J. A. McCleverty and T. J. Meyer (Eds.), Comprehensive Coordination Chemistry II, Elsevier Ltd, Amsterdam, 2003, pp. 97-115.

[16] Y. Lin, N. G. Smart and C. M. Wai, Supercritical fluid extraction and chromatography of metal chelates and organometallic compounds, TrAC. 14 (1995) 123-133. https://doi.org/10.1016/0165-9936(95)94045-G.

[17] Y. Lin and C. M. Wai, Supercritical Fluid Extraction of Lanthanides with Fluorinated B-Diketones and Tributyl Phosphate, Anal. Chem. 66 (1994) 1971-1975. https://doi.org/10.1021/ac00085a008.

[18] C. M. Wai and B. Waller, Dissolution of Metal Species in Supercritical Fluids Principles and Applications, Ind. Eng. Chem. Res. 39 (2000) 4837-4841. https://doi.org/10.1021/ie0002879

[19] K. N. Vidhate, U. P. K. Shaikh, B. R. Arbad and M. K. Lande, Extraction and separation studies of gold(III) with 4-(4-methoxybenzylideneimino)-5-methyl-4H-1,2,4- triazole-3-thiol in hydrochloric acid medium, J. Saudi Chem. Soc. 19 (2015). 54-58. https://doi.org/10.1016/j.jscs.2011.12.018

[20] J. C. Yannopoulos, The Extractive Metallurgy of Gold, first ed., Van Nostrand Reinhold, New york, 1991.

[21] S. Syed, Recovery of gold from secondary sources - A review, Hydrometallurgy, (2012) 30-51. https://doi.org/10.1016/j.hydromet.2011.12.012

[22] A. Aydin, E. Kaki and A. A. Aydin, Gold leaching by use of an n,n′-disubstituted thiourea, Sep Sci Technol. 36 (2001) 3239-3251. https://doi.org/10.1081/SS-100107770

[23] Y. A. Zolotov, O. M. Petrukhin, V. N. Shevchenko, V. V. Dunina and E. G. Rukhadze, Solvent extraction of noble metals with derivatives of thiourea, Anal. Chim. Acta. 100 (1978) 613-618. https://doi.org/10.1016/S0003-2670(01)93355-0.

[24] J. D. Glennon, S. J. Harris, A. rtalker, C. C. McSweeney and M. O'Connell, Carrying Gold in Supercritical C0$_2$, Gold Bulletin, 32 (1999) 52-58.

[25] P. Wasserscheid and T. Welton, Ionic Liquids in Synthesis, second ed., WILEY-VCH Verlag GmbH & Co, Weinheim, 2008.

[26] E. A. Oraby and J. J. Eksteen, The leaching of gold, silver and their alloys in alkaline glycine–peroxide solutions and their adsorption on carbon, Hydrometallurgy. 152 (2015) 199–203. https://doi.org/10.1016/j.hydromet.2014.12.015.

[27] J. A. Whitehead, G. A. Lawrance and A. McCluskey, Green' leaching: recyclable and selective leaching of gold-bearing ore in an ionic liquid, Green Chemistry, 6 (2004) 313-315. http://dx.doi.org/10.1039/B406148A

[28] G.-c. Tian, L. Jian and Y.-x. Hua, Application of ionic liquids in hydrometallurgy of nonferrous metals, Trans. Nonferrous Met. Soc. 20 (2010) 13 – 520. https://doi.org/10.1016/S1003-6326(09)60171-0.

[29] S. Mekki, C. M. Wai, I. Billard, G. Moutiers, J. Burt, B. Yoon, J. S. Wang, C. Gaillard, A. Ouadi and P. Hesemann, Extraction of Lanthanides from Aqueous Solution by Using

RoomTemperature Ionic Liquid and SupercriticalCarbon Dioxide in Conjunction, Chem. Eur. J. 12 (2006) 1760 – 1766. https://doi.org/10.1002/chem.200500559.

[30] C. M. Wai, Y.-J. Liao, W. Liao, G. Tian, R. S. Addleman, D. Quacha and S. P. Pasilis, Uranium dioxide in ionic liquid with a tri-n-butylphosphate–HNO3 complex-dissolution and coordination environmen, Dalton Transanctions. 40 (2011) 5039–5045. https://doi.org/10.1039/C0DT01518K

[31] J. S. Wang, C. N. Sheaff, B. Yoon, R. S. Addleman and C. M. Wai, Extraction of Uranium from Aqueous Solutions by Using Ionic Liquid and Supercritical Carbon Dioxide in Conjunction, Chem. Eur. J. 15 (2009) 4458 – 4463. https://doi.org/10.1002/chem.200801415

[32] L. A. Blanchard, Z. Gu and J. F. Brennecke, High-Pressure Phase Behavior of Ionic Liquid/CO2 Systems, J. Phys. Chem. B. 105 (2001) 2437-2444. https://doi.org/10.1021/jp003309d.

[33] J. W. Hutchings, K. L. Fuller, M. P. Heitz and M. M. Hoffmann, Surprisingly high solubility of the ionic liquid trihexyltetradecylphosphonium chloride in dense carbon dioxide, Green Chemistry, 7 (2005) 475–478. https://doi.org/10.1039/B502204E.

[34] G. Li, D. Zhou, Q.-Q. Xu, G.-Y. Qiao and J.-Z. Yin, Solubility of Ionic Liquid [Bmim]Ac in Supercritical CO_2 Containing Different Cosolvents, J. Chem. Eng. Data. 63 (2018) 1596−1602. https://doi.org/10.1021/acs.jced.7b01108.

[35] W. Wu, J. Zhang, B. Han, J. Chen, Z. Liu, T. Jiang, J. He and W. Li, Solubility of room-temperature ionic liquid in supercritical CO2 with and without organic compounds, ChemComm, (2003) 1412–1413. https://doi.org/10.1039/B302311G.

[36] G. Mawire, L. VanDyk, Extraction of Scandium (Sc) Using a Task-Specific Ionic Liquid Protonated Betaine Bis(Trifluoromethylsulfonyl)Imide [Hbet][Tf2N], In: Davis B. et al. (eds), Extraction2018-The Minerals, Metals & Materials Series, Springer, 2018, pp 2723-2734. https://doi.org/10.1007/978-3-319-95022-8_230

[37] L. K. Sinclair, D. L. Baek, J. Thompson, J. W. Tester and R. V. Fox, Rare earth element extraction from pretreated bastnäsite in supercritical carbon dioxide, J. Supercrit. Fluids, 124 (2017) 20–29. https://doi.org/10.1016/j.supflu.2017.01.005.

[38] K. E. Laintz and E. Tachlkawa, Extraction of Lanthanides from Acidic Solution Using Tributyl Phosphate Modified Supercritical Carbon Dioxide, Anal. Chem. 66 (1994) 2190-2193. https://doi.org/10.1021/ac00085a040.

[39] M. D. Samsonov, C. M. Wai, S.-C. Lee, Y. Kulyakob and N. G. Smart, Dissolution of uranium dioxide in supercritical fluid carbon dioxide, Commun. Chem. (2001) 1868–1869. https://doi.org/10.1039/B103468P.

[40] O. Tomioka, Y. Meguro, Y. Enokida, I. Yamamoto and Z. Yoshida, Dissolution Behavior of Uranium Oxides with Supercritical CO_2 Using HNO_3-TBP Complex as a Reactant, J Nucl Sci Technol. 38 (2001) 1097-1102. https://doi.org/10.1080/18811248.2001.9715141

[41] Y. Enokida, I. Yamamoto and C. M. Wai, Extraction of Uranium and Lanthanides from Their Oxides with a High-Pressure Mixture of TBP-HNO_3- H_2O-CO_2, In: A. S. Gopalan, C. M. Wai and H. K. Jacobs (Eds.), Supercritical Carbon Dioxide Separations and Processes, American Chemical Society., Washington, D C, 2003, pp. 10-22.

[42] B. A. Wills, Wills' Mineral Processing: An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery, seventh ed., Elsevier Ltd, Amsterdam, 2006.

[43] M. D. Adams, Advances in gold ore processing, first ed., Elsevier, Amsterdam, 2005.

[44] C. D. Barton and A. D. Karathanasis, Clay minerals, In: R. Lal, Ed. Encyclopedia of Soil Science, Marcel Dekker., New York, 2002, pp. 187-192.

[45] F. K. Crundwel, The mechanism of dissolution of minerals in acidic and alkaline solutions: Part II Application of a new theory to silicates, aluminosilicates and quartz, Hydrometallurgy, 149 (2014) 265–275. https://doi.org/10.1016/j.hydromet.2014.07.003

[46] C. J. vanOss and R. F. Giese, The Hydrophilicity and Hydrophobicity of Clay Minerals, Clays Clay Miner. 43 (1995) 474-477. https://doi.org/10.1346/CCMN.1995.0430411

[47] Y. I. Tarasevich and E. V. Aksenenko, Hydrophobicity of Talc Basal Surface, J. Colloid Sci. 76 (2014) 483–489. https://doi.org/10.1134/S1061933X14040140

[48] S. Mohammadnejad, J. L. Provis and J. S. J. v. Deventer, Effects of grinding on the preg-robbing behaviour of pyrophyllite, Hydrometallurgy, 146 (2014) 154–163. https://doi.org/10.1016/j.hydromet.2014.04.007

[49] B. Onghena and K. Binnemans, Recovery of Scandium(III) from Aqueous Solutions By Solvent Extraction with the Functionalized Ionic Liquid Betainium Bis(trifluoromethylsulfonyl)imide, Ind. Eng. Chem. Res. (2015) 1887-1898. https://doi.org/10.1021/ie504765v

[50] T. V. Hoogerstraete, B. Onghena and K. Binnemans, Homogeneous Liquid–Liquid Extraction of Rare Earths with the Betaine—Betainium Bis(trifluoromethylsulfonyl)imide Ionic Liquid System, Int. J. Mol. Sci. 14 (2013) 21354-21377. https://doi.org/10.3390/ijms141121353.